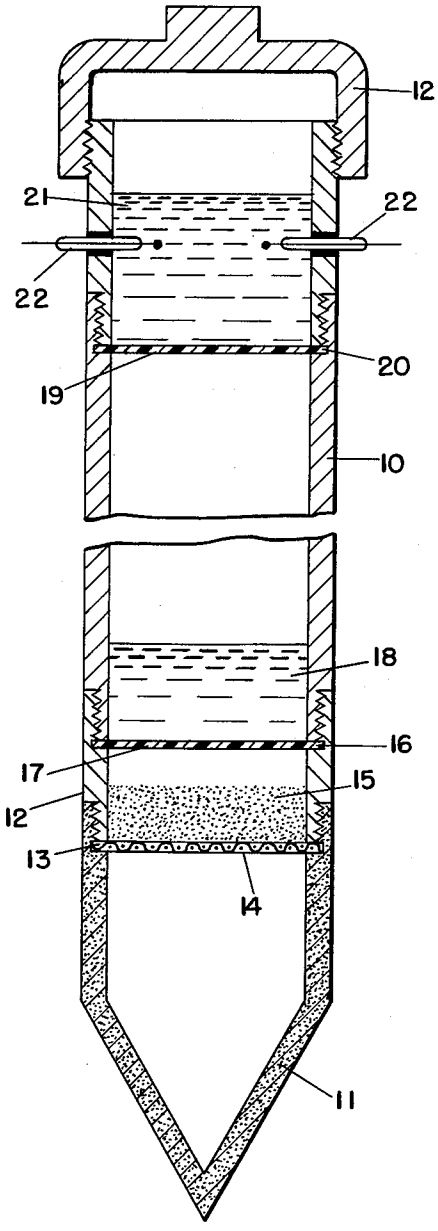
April 3, 1962 P. E. OBERDORFER, JR., ETAL 3,028,313

GEOBIOCHEMICAL PROSPECTING

Filed March 7, 1960



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United States Patent Office 3,028,313 Patented Apr. 3, 1962

3,028,313

GEOBIOCHEMICAL PROSPECTING

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Filed Mar. 7, 1960, Ser. No. 13,279
4 Claims. (Cl. 195—103.5)

This invention relates to geobichemical prospecting for petroleum by utilizing methane-consuming microorganisms capable of growing adjacent to earth sites containing methane.

Methods of geochemical prospecting for petroleum have been proposed heretofore wherein samples of earth from selected sites have been analyzed for one or more light hydrocarbons. It has been postulated that hydrocarbon gases migrate through the earth from subterranean petroleum reservoirs and hence are present in the earth near the surface in the vicinity of petroleum deposits. Determination of amounts of one or more light hydrocarbons in soil samples taken from selected locations thus is thought to provide a means for indicating the proximity of petroleum. However, it has generally been considered that the content of methane in earth samples is unreliable for indicating emanations of hydrocarbons from petroleum reservoirs, since methane can also be present as a result of vegetative decomposition. For this reason it usually has been preferred to analyze the soil samples for ethane, propane and/or butane. Since the amount of any of these hydrocarbons which might be present in a soil sample as a result of migration from a petroleum formation would be extremely small in any event, errors in analysis can readily vitiate the results and render the procedure unreliable.

It has also been proposed to analyze soil samples by burning contained organic matter to form carbon dioxide, converting the carbon dioxide to barium carbonate or the like and then determine in the barium carbonate the ratio of carbon having an atomic weight of 14 to carbon having an atomic weight of 12 by measuring the extent of radioactivity derived from C^{14}. Such ratio for carbon derived from petroleum would be low, since the age of petroleum is sufficient for most of the radioactive C^{14} to have disappeared; whereas the ratio would be relatively high for the carbon of more recent vintage derived from vegetation. Hence, an analysis of a soil sample showing an anomalously low C^{14} to C^{12} ratio would be an indication that the sample was taken from a locus in proximity to a petroleum deposit. This procedure, however, is also of dubious reliability for several reasons. For example, the soil sample may contain substantial amounts of non-gaseous organic matter derived from vegetation and having a high C^{14} to C^{12} ratio while also containing a relatively small but otherwise significant amount of gaseous hydrocarbon derived from petroleum and hence having a low C^{14} to C^{12} ratio. In such case the relatively high amount of vegetative carbon would mask out the effect of the small but significant amount of petroleum hydrocarbon in the radioactivity test, resulting in an erroneous conclusion as to the proximity of petroleum. Also, even if the sample contained no solid organic matter while containing low boiling hydrocarbons, the amount of such hydrocarbons would be small in any event and thus the C^{14} present would be extremely small regardless of the hydrocarbon source. Hence great difficulty would be encountered in securing reliable analytical results.

A still further petroleum prospecting procedure proposed in the prior art involves exposing soil samples in the presence of a biological nutrient and at an incubating temperature to an atmosphere of oxygen and a hydrocarbon, e.g. ethane, in which the carbon has an atomic weight

of 14 and hence is radioactive. This procedure is based on the concept that soil containing hydrocarbons that have migrated from a petroleum deposit will also contain bacteria which consume such hydrocarbons. Hence, such bacteria should grow when the sample is maintained under the laboratory incubating conditions in the presence of the selected hydrocarbon in which the carbon is the radioactive C^{14}, and the rate of growth can be ascertained by determining the intensity of the radioactivity produced. The rate of growth is taken as a measure of the amount of hydrocarbon-consuming bacteria present in the original soil sample, which in turn is taken as an indicium of the proximity of petroleum to the site of sampling. The value of this method is also questionable, since it is based on the assumption that soil containing hydrocarbons which have migrated from a petroleum deposit of necessity contains an amount of hydrocarbon-consuming bacteria proportional to the hydrocarbon concentration in the soil. There are numerous factors other than hydrocarbon concentration, however, which will affect the growth of the bacteria in the soil, e.g. the mineral nutrient values available, oxygen availability, acidity of the soil and temperature. Accordingly, it is possible to have a significant amount of migrated hydrocarbons present in the soil while having essentially no hydrocarbon-consuming bacteria. Hence, the dependability of the last discussed method in locating petroleum deposits likewise is at least doubtful.

The present invention is directed to a novel geobiochemical method of prospecting which avoids the objections to the prior art methods discussed above and provides a distinct improvement in the art of petroleum prospecting. According to one embodiment of the invention, a culture of methane-consuming micro-organisms is placed adjacent the earth at a selected locus beneath the surface and the culture is allowed to remain there for a time sufficient to permit substantial growth of the micro-organisms if any methane is present in the soil. Thereafter the culture is removed from the earth and the radioactivity of the micro-organism residue is determined to ascertain the ratio of C^{14} to C^{12} in the methane consumed. Carbon derived from methane from vegetation will have a high C^{14} to C^{12} ratio while carbon derived from methane which emanated from a petroleum reservoir will have a low ratio. Hence an anomalously low ratio of C^{14} to C^{12} will serve as an indicium of the proximity of a petroleum deposit.

The prospecting method according to the present invention in effect utilizes the methane-consuming ability of certain micro-organisms to concentrate the carbon from methane present in the soil at the selected site. When methane is present in the soil, it will continuously diffuse therefrom to the micro-organism culture and a sufficiently long time, e.g. one month or more, can be allowed for a substantial amount of the methane to be consumed. Hence, the method does not depend upon analyzing accurately for more or less trace amounts of hydrocarbon, such as is required if a soil sample itself is analyzed. Furthermore, the present method permits methane to be utilized as the hydrocarbon that indicates the proximity of petroleum by employing an analysis procedure that distinguishes between methane from such source and methane from vegetation. This is distinctly advantageous, since methane is the hydrocarbon component which will most readily diffuse from a petroleum reservoir.

It is known that some strains of micro-organisms can, in the presence of oxygen, grow on methane as the sole organic material that enters into the metabolism. Certain bacterial species of the Pseudomonad genus, particularly *Pseudomonas methanica* and related species, are an example. Also, certain species of the Mycobacterium genus

can utilize methane as their only food element. Bacteria of these types and any other micro-organisms whose metabolism is specific for methane can be employed in practicing the present invention.

In practicing the invention a culture of a suitable strain of methane-consuming micro-organisms is prepared and is placed adjacent the earth at a site desired to be tested so that it can come in contact with any methane emanating from the soil. The culture either can be in liquid form or can be carried on a non-organic solid culture medium such as silica gel. In either case suitable mineral nutrients including phosphorous and nitrogen must be present to permit growth of the micro-organisms. A particularly suitable culture composition is as follows:

Ingredient:	Parts by weight
KNO_3	1.0
$Na_2HPO_4 \cdot 12H_2O$	0.53
KH_2PO_4	0.09
$MgSO_4 \cdot 7H_2O$	0.20
$FeSO_4 \cdot 7H_2O$	0.001
Distilled water	1000

The medium is prepared by dissolving the inorganic salts in water and sterilizing the solution for 20 minutes with steam at a pressure of 20 p.s.i.g. For maximum rate of growth of the micro-organisms the pH of the culture medium should be between 6.8 and 8.0. The culture can be placed in a bag made of material through which methane and oxygen can readily diffuse, e.g. polyethylene, polypropylene or other synthetic resin, and the bag can be buried in the earth at a suitable depth or disposed within a borehole sealed at the earth surface. Alternatively, the culture can be placed in a suitable container above ground and gases can be pumped from a borehole in the earth and into the container wherein contact with the culture is effected.

After the micro-organism colony has had sufficient opportunity to feed on methane from the soil to insure substantial growth if methane is present, the microbial residue is then tested for radioactivity under standardized conditions. This can be done by direct measurement of the radioactivity of a weighed amount of the micro-organism after separation from the culture medium and drying, the measurement being made by a Geiger-Muller counter or a scintillation counter. However, it is preferable to convert the microbial carbon into carbon dioxide by burning which in turn is converted to barium carbonate by absorption in a barium hydroxide solution, then separate and dry the barium carbonate and measure the radioactivity of a weighed amount of this material. An anomalously low radioactivity is an indication that methane consumed by the organisms was derived from petroleum.

The accompanying drawing is a vertical section of an apparatus for practicing the invention in a preferred manner. The drawing illustrates a device for holding a culture of the methane-consuming micro-organisms, which device can be inserted into the ground to an appropriate depth and which is so constructed that methane and oxygen from the soil can diffuse to the culture to cause growth of micro-organisms. More specifically, the device comprises an elongated housing **10** formed from threaded tubing which is connected to a pointed bottom closure member **11** and a cap **12** at the top. The bottom member **11** is constructed of a rigid porous material such as sintered metal or hard sintered resin, so that gases from the earth can diffuse through the wall and enter the housing. Bottom member **11** is threaded to a ring **12** and a screen **14** is held between the two pieces at shoulder **13**. The screen is used for supporting a bed **15** of a suitable absorbent for carbon dioxide, for example, a hydrous caustic soda supported on asbestos and sold commercially under the proprietary name "Ascarite." Ring **12** is threaded to tube **10**, and a membrane **17** is held between the abutting shoulders at **16**. Membrane **17** serves to support the culture medium **18** which contains the methane-consuming micro-organisms. The membrane **17** is made of a material through which both methane and oxygen can readily diffuse. Examples of such material are polyethylene, polypropylene and other synthetic organic resins.

Another membrance **19** is positioned between abutting shoulders **20** of the tube **10** and the top portion of the device. This membrane, which can also be made of polyethylene or other synthetic resins, will allow carbon dioxide to diffuse through it. Membrane **19** is used as a support for an absorbent capable of absorbing carbon dioxide, which in this case preferably is an aqueous solution of barium hydroxide as shown at **21**. A pair of insulated electrodes **22** are positioned in packing glands in the upper wall of the device so as to be immersed in the aqueous solution. These electrodes are employed for determining any changes in the electrical conductivity of the barium hydroxide solution and thus indicating whether or not any change in the barium hydroxide concentration has occurred.

In using the illustrated apparatus for petroleum prospecting, the device containing the necessary materials is assembled as described above and then is forced into the ground at a selected site. The length of the device should be such that the porous lower portion **11** is located at a desired depth which is generally several feet beneath the earth surface, with the electrodes **22** being above ground level. By means of suitable apparatus (not shown), the initial conductivity of the barium hydroxide solution **21** is measured through electrodes **22**. The device is then permitted to remain in the ground so that gases contained therein can diffuse through porous member **11** and into absorbent bed **15**. Upon contact with the absorbent, any carbon dioxide present will be absorbed. Such removal of carbon dioxide in effect acts as a pumping means which aids in the diffusion of gases into the device.

After passing through the absorbent bed **15**, oxygen and methane if present will diffuse through membrance **17** and be absorbed in the liquid culture medium **18**. This causes growth of the micro-organism colony the rate of which depends upon the amount of methane entering the culture medium. Carbon dioxide is formed as a by-product of the metabolism, and this product will diffuse out of the culture medium solution and be released into the chamber thereabove. Accordingly, carbon dioxide produced by the micro-organisms will contact membrane **19** which, as previously described, is constructed so as to allow diffusion of carbon dioxide through it. The carbon dioxide thus will be absorbed by the barium hydroxide solution and will react to form insoluble barium carbonate. Precipitation of the carbonate salt will cause a change in conductivity of the solution. Hence, by simply measuring the conductivity of the solution from time to time, it can be determined whether or not methane has entered the device and caused growth of the bacteria without any necessity for removing the device from the ground and opening it for inspection. If after a sufficient lapse of time no growth is indicated, it is then known that proximity of petroleum is not indicated; and the device can be withdrawn and taken to another location for further prospecting.

In cases where substantial bacterial growth is shown by the conductivity measurement, the device is then removed from the ground for radioactivity tests. These tests can be made on either the precipitated barium carbonate or the micro-organism residue or both. Testing of a weighed amount of the barium carbonate after drying is particularly convenient. When the tests show an anomalously low radioactivity, it is known that the ratio of C^{14} to C^{12} in the metabolism products is low and hence that at least a substantial proportion of the methane consumed by the microorganisms was derived from petroleum. This thus serves as an indication that the site where the

device was located is in the vicinity of a petroleum deposit.

Various modifications of the above-described device can be made. For example, with the device as shown in the drawing, part of the carbon dioxide resulting from the micro-organism metabolic process may diffuse from the culture medium downwardly through membrane **17** and be absorbed in the absorbent bed **15** along with any carbon dioxide which may have entered the device from the surrounding soil. In some instances it may be desirable to convert all of the carbon dioxide produced by the metabolism into barium carbonate and determine the total amount of barium carbonate formed for purpose of quantitatively indicating the rate of growth of the micro-organisms. In such cases membrane **17** can be constructed of material through which methane and oxygen can diffuse but not carbon dioxide. This will cause all of the carbon dioxide to diffuse upwardly to the barium hydroxide solution at **21**. Alternatively, another barium hydroxide bath can be provided on a membrane positioned between absorbent bed **15** and membrance **17**, so that any carbon dioxide which diffuses downwardly from the culture medium will react therewith and be precipitated as barium carbonate. With this modification, the total amount of barium carbonate formed in both the upper and lower baths subsequently could be determined and utilized as a measure of the rate of micro-organism growth.

The present invention can also be used for prospecting adjacent the floor of an ocean, sea, lake, river or the like. In such case a bag made of polyethylene or other suitable resin is filled with a liquid culture medium containing methane-consuming micro-organisms and the bag is lowered on a wire or rope to the floor of the ocean. If methane is present in the water, it along with oxygen which is also present will diffuse from the water through the wall of the bag and will dissolve in the culture medium, thus causing growth of the micro-organisms. The by-product carbon dioxide formed by the metabolism process will largely remain dissolved in the culture medium due to the hydrostatic pressure and will diffuse through the wall of the bag into the surrounding water. After the bag has remained immersed for sufficient time to permit substantial growth, the bag is removed and radioactivity tests are made as previously described to determine whether at least some of the methane consumed was derived from petroleum.

We claim:

1. Method of geobiochemical prospecting for petroleum deposits which comprises placing a culture of methane-consuming micro-organisms adjacent the earth at a selected locus, permitting said micro-organisms to grow at the selected locus by feeding on methane emanating from adjacent earth, and thereafter determining the radioactivity of the micro-organisms as an indication of the ratio of C^{14} to C^{12} in the methane consumed, whereby an anomalously low ratio serves as indicium of the proximity of petroleum.

2. A device for geobiochemical prospecting for petroleum which comprises an elongated housing having a pointed and porous bottom portion through which methane and oxygen can diffuse, a transverse porous support thereabove adapted to support a bed of material capable of absorbing carbon dioxide, a transverse membrane above said support adapted to hold a culture of methane-consuming micro-organisms and capable of permitting diffusion of methane and oxygen to the culture, a second transverse membrane thereabove capable of permitting diffusion of carbon dioxide therethrough and adapted to support an aqueous solution of a compound capable of reacting with carbon dioxide to form a precipitate, and a pair of electrodes positioned for immersion in the aqueous solution for indicating changes in electrical conductivity thereof.

3. Method of geobiochemical prospecting for petroleum deposits which comprises placing a culture of methane-consuming micro-organisms adjacent the earth at a selected locus, permitting said micro-organisms to grow at the selected locus by feeding on methane emanating from adjacent earth, and thereafter determining the radioactivity of carbon contained in the carbon dioxide resulting from metabolism of the micro-organisms as an indication of the ratio of C^{14} to C^{12} in the methane consumed, whereby an anomalously low ratio serves as indicium of the proximity of petroleum.

4. Method of geobiochemical prospecting for petroleum deposits which comprises placing a culture of methane-consuming micro-organisms adjacent the earth at a selected locus, permitting said micro-organisms to grow at the selected locus by feeding on methane emanating from adjacent earth, reacting carbon dioxide produced by metabolism of the micro-organisms with an aqueous solution containing a compound reactive with carbon dioxide to form a precipitate, and thereafter determining the radioactivity of a product of the micro-organism metabolism as an indication of the ratio of C^{14} to C^{12} in the methane consumed, whereby an anomalously low ratio serves as indicium of the proximity of petroleum.

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